PORTLAND HARBOR RI/FS

REMEDIAL INVESTIGATION REPORT

APPENDIX D5.3
PATTERNS AND TRENDS OF PCBS, PCDD/FS, DDX, AND PAHS IN BIOTA

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APPENDIX D5.3 PATTERNS AND TRENDS OF PCBS, PCDD/FS, DDX, AND PAHS IN BIOTA

D5.3.1 Introduction

In addition to the other indicator contaminants, Section 5.6 of the remedial investigation (RI) report discusses the concentrations of four grouped indicator contaminants: polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs), DDx[1], and polycyclic aromatic hydrocarbons (PAHs) in biota. This appendix provides additional details on the nature of these four contaminant groups in biota by examining the patterns in their constituent chemicals. The detail provided here helps inform discussion of the conceptual site model (Section 10) and identification of potential sources and contaminant transport.

Stacked bar charts, designed to reveal potential distinctive patterns in the relative abundance of components (e.g., homologs, isomers), are used to examine the nature of contaminants in this appendix. Figures D5.3-1 through D5.3-7 show the distribution of PCB homologs, PCDD/F homologs, and individual components of total DDx in each sample, and the distribution of PAHs in clam samples. The analyte components are shown in the stacked bars as a percent of the total concentration, while the total concentration of the indicator contaminant is displayed as a line on a logarithmic scale. Sample type and ID labels are provided on the x-axis, and river mile is indicated on the secondary x-axis along the top of the chart.[2]

D5.3.2 Patterns and Trends of PCBs in Biota

Fish assimilate and metabolize different PCB congeners at different rates; therefore, the PCB pattern in fish tissue may not closely resemble the pattern of the Aroclor that was released into the river or of the standard used by the laboratory to identify and quantify the PCBs in the sample. The limitations of the Aroclor analysis are described in Appendix D1.4. Because of the uncertainties related to Aroclor identification and because PCB congeners were analyzed in most of the tissue samples used for the Portland Harbor RI, PCB patterns in tissue are described only in terms of homologs (i.e., congeners grouped according to chlorination level).

PCBs were detected in all fish samples from the Study Area. Although PCB homolog composition varied throughout the river, tetrachlorobiphenyls (tetraCBs),

[1] DDx represents the sum of the 2,4'- and 4,4'- isomers of dichloro-diphenyl-dichloroethane (DDD), dichloro-diphenyl-dichloroethene (DDE), and dichloro-diphenyl-trichloroethane (DDT).

[2] It is important to note that patterns apparent in the stacked bar charts should be interpreted with caution. Changes in chemical composition and apparent trends shown by the bar charts may be indicative of significant patterns (e.g., distinctive source contributions), or they may be within the range of normal data variability. Source identification and allocation are complex multivariate problems. The pattern shifts discussed here based on stacked bar chart presentations may be suggestive, but cannot be interpreted directly as or attributed to localized sources. Such a characterization would require rigorous quantitative forensic analysis, which is outside the scope of this RI/FS.

pentachlorobiphenyls (pentaCBs), hexachlorobiphenyls (hexaCBs), and heptachlorobiphenyls (heptaCBs) were typically present in proportions greater than 10 percent (Figure D5.3-1). HexaCBs and heptaCBs were generally dominant in fish tissue samples from throughout the Study Area. Monochlorobiphenyls (monoCBs), dichlorobiphenyls (diCBs), and nonachlorobiphenyls (nonaCBs) were very rare, while trichlorobiphenyls (triCBs) and octachlorobiphenyls (octaCBs) were rare in comparison to the other homologs. For many fish species, more highly chlorinated PCB homologs appear to be seen more frequently in the upper reaches of the Study Area than in the lower third.

PCBs were detected in all invertebrate samples from the Study Area that were analyzed for PCB congeners. PCBs were not detected in 10 crayfish tissue composites that were only analyzed for Aroclors, which have a higher detection limit than PCB congeners. Among PCB homologs in invertebrate samples, tetraCBs, pentaCBs, hexaCBs, and heptaCBs were most abundant overall, appearing similar to the fish tissue samples (Figure D5.3-2). Laboratory-exposed clams were distinctive in appearing to contain a relatively large fraction of diCBs, which were present in relatively lower percentages in field-collected clams from the same locations, with the exception of location FC027 Rep 1 (RM 8.7E). PCB patterns in crayfish varied widely. In particular, the PCB pattern in crayfish sample 06R031 (RM 6.8E) is notable for its apparently high percentage of monoCBs and diCBs and relatively low content of triCBs, tetraCBs, and pentaCBs. The PCB pattern in clams and worms exposed at the laboratory to sediments from three locations (BT002 at RM 2.3E, BT017 at RM 6.9W, and BT028 at RM 8.8W) appeared to contain distinctly higher levels of tetraCBs and lower levels of hexaCBs and heptaCBs than the remaining samples. This pattern was reflected only slightly in field-collected clam samples from these locations.

As in the Study Area, PCB congeners in fish samples from the upriver reach and above-falls locations included predominantly tetraCBs, pentaCBs, hexaCBs, and heptaCBs. Chlorination levels were lower for juvenile Chinook and juvenile lamprey than for brown bullhead and smallmouth bass: juvenile Chinook and juvenile lamprey contained higher proportions of triCBs and tetraCBs, whereas brown bullhead and smallmouth bass contained more heptaCBs and octaCBs. Upstream invertebrate samples returned few detected congener results; therefore, the patterns in these samples were not examined.

D5.3.3 Patterns and Trends of Total PCDD/F Homologs and TCDD TEQ in Biota

PCDD/Fs were detected in all fish tissue samples from the Study Area. The homolog distribution in fish tissues was quite variable, with differences evident between species as well as between locations and tissue types within species (Figure D5.3-3). In carp, juvenile lamprey, and sculpin tissues with total PCDD/Fs concentrations above 50 pg/g, octachlorodibenzo-p-dioxin (OCDD) tended to dominate many of the samples, with secondary dominance shown variously by hexachlorodibenzo-p-dioxins (HxCDDs), heptachlorodibenzo-p-dioxins (HpCDDs), tetrachlorodibenzofurans (TCDFs),

pentachlorodibenzofurans (PeCDFs), and hexachlorodibenzofurans (HxCDFs). In smallmouth bass samples with total PCDD/Fs concentrations above 50 pg/g, PCDD/F patterns were dominated by PeCDFs and TCDFs. Overall, smallmouth bass were notable for the apparent dominance of TCDFs and PeCDFs and relatively low levels of HpCDDs and OCDD at many locations compared to other fish species from the Study Area. Round 3 sturgeon, which were individual whole-body samples, were dominated by TCDFs. The PCDD/F patterns for sturgeon samples from the ODHS/USEPA/ATSDR Fish Contaminant Study (ODHS, EPA, and ASTDR 2003), which were fillet samples, appear distinctly different from Round 3 whole-body sturgeon.

As in the Study Area, dioxin and furan homolog patterns varied among species, locations and individual samples in fish tissue from upstream areas. For example, TCDFs dominated the PCDD/F pattern for juvenile lamprey from above the falls, whereas OCDD was the predominant homolog for juvenile lamprey from the upriver reach area (below the falls); OCDD was also clearly the dominant homolog in juvenile Chinook. Smallmouth bass contained a high proportion of PeCDF in many cases, whereas HxCDD was the most abundant homolog in two of the three brown bullhead samples. One brown bullhead sample was notable for its large proportion of TCDD (30 percent of total PCDD/Fs as the sum of homologs); this homolog did not account for more than 10 percent of the PCDD/Fs in any other sample from the upriver reach or above the falls. Additional differences were noted among samples from the same species and similar locations.

PCDD/Fs were detected in all invertebrate tissue samples from the Study Area. The PCDD/F homolog distribution was more consistent across invertebrate species than fish tissue species in that OCDD was often the most abundant homolog, usually followed by TCDFs and HpCDDs. Pentachlorodibenzo-p-dioxins (PeCDDs), HxCDDs, heptachlorodibenzofurans (HpCDFs), and OCDF tended to be the least abundant homolog groups (Figure D5.3-4). Distinct homolog patterns seemed to be present in many samples that contained higher total PCDD/Fs concentrations than typically found for each invertebrate sample type. Apparently unique signatures were seen in every species and in several locations. For example, various invertebrate samples collected from the vicinity of RM 7W exhibited a visually unique PCDD/F pattern, including field-collected and laboratory-exposed clam and worm samples from BT017 and BT018 and crayfish from location 07R006. TCDFs were the most abundant group in these samples, followed by PeCDFs. Among epibenthic samples, MIT003/005/006 (multiplate samples from RM 6.5–7.4) appeared to have an unusual pattern, with TCDFs most abundant, followed by OCDD. The PCDD/F pattern in crayfish from location 08R003 (RM 8W, near the mouth of Swan Island Lagoon) was also unusual, with PeCDFs dominant, followed by OCDD and TCDFs. Additional apparently unique patterns were found in various samples from other locations (Figure D5.3-4). PCDD/F analyses were not conducted on the invertebrate samples from outside of the Study Area.

D5.3.4 Patterns and Trends of DDx Compounds in Biota

DDx compounds were detected in all fish tissue samples from the Study Area. 4,4'-DDE accounted for more that 50 percent of the total DDx concentration in fish tissues, with

some exceptions (Figure D5.3-5). DDDs constituted 25 percent or more of the total DDx in various samples of sculpin, carp, largescale sucker, juvenile Chinook, juvenile lamprey, and smallmouth bass, particularly in fishing areas from RM 3 to 9. In many of the sculpin samples and in juvenile Chinook samples from T01 (RM 3.4E) and T03 (RM 9.7W), 4,4'-DDT dominated; and in juvenile Chinook samples from T02 (RM 6.9W), 4,4'-DDD dominated the three whole-body composite samples.

In fish upstream of the Study Area, the most abundant isomer in all tissues was 4,4'-DDE, which accounted for at least 50 percent and up to 85 percent of the total DDx. Typically 4,4'-DDT was the next most abundant; all other DDx compounds were also present at varying levels.

DDx compounds were detected in all invertebrate tissue samples from the Study Area. In general, 4,4'-DDD and 4,4'-DDE were the dominant isomers in invertebrate tissues (Figure D5.3-6). Crayfish DDx profiles were dominated by 4,4'-DDE or various other DDx compounds, depending on location. Laboratory-exposed clam samples from the U.S. Army Corps of Engineers investigation (Tetra Tech 2006) also had a high percentage of 4,4'-DDT; however, the 2,4'-isomers of the DDx compounds were generally not detected in these samples, resulting in the absence of data for 2,4'-DDD and a shift in the apparent DDx pattern.

Three invertebrate samples (one of juvenile Chinook stomach content, one of laboratory-exposed worm tissue, and one of laboratory-exposed clam tissue) from the upriver reaches were analyzed for DDx isomers. In the stomach content sample, the most abundant isomer was 4,4'-DDE, which contributed over 80 percent to the total DDx concentration. In worms, 4,4'-DDE and 2,4'-DDT were the two most abundant isomers; in the laboratory-exposed clams, 4,4'-DDE, 4,4'-DDT, and 2,4'-DDT were most abundant.

D5.3.5 Patterns and Trends of PAHs in Clam Tissue

PAH patterns were examined only in clam tissue associated with sediment from the Study Area. PAHs were detected in all clam tissue samples collected from the Study Area or exposed to sediment from the Study Area.

Clam tissue from the Study Area generally contained relatively higher proportions of phenanthrene, fluoranthene, pyrene, and chrysene, with lesser proportions of benzo(a)anthracene. Low-molecular-weight polycyclic aromatic hydrocarbons (LPAHs) other than phenanthrene and the five- and six-ring high-molecular-weight polycyclic aromatic hydrocarbons (HPAHs) (see Table 5.1-7) were generally present but not prevalent (Figure D5.3-7). Naphthalene and dibenzo(a,h)anthracene were each detected in only a few samples, but naphthalene was the dominant PAH in the field-collected, undepurated clam from location CA12E (RM 12.1E; sample LW3-CA12E-C00). Naphthalene was not detected in the depurated clam sample from this location. Additional samples with PAH patterns that appeared to differ from surrounding areas included field-collected clams from locations FC014 (RM 5.9W), FC015 (RM 6.4W), and FC025 (RM 8.5W), and laboratory-exposed clams for locations WR-VC-29 (RM 7.7, just downstream of Swan Island Lagoon in the navigation channel), BT026 (RM 8.5E, in Swan Island Lagoon), and BT031 (RM 9.5E). PAH patterns in three field-collected clam samples

from Round 1 were obscured by non-detects; only fluoranthene and pyrene were detected in two of these samples.

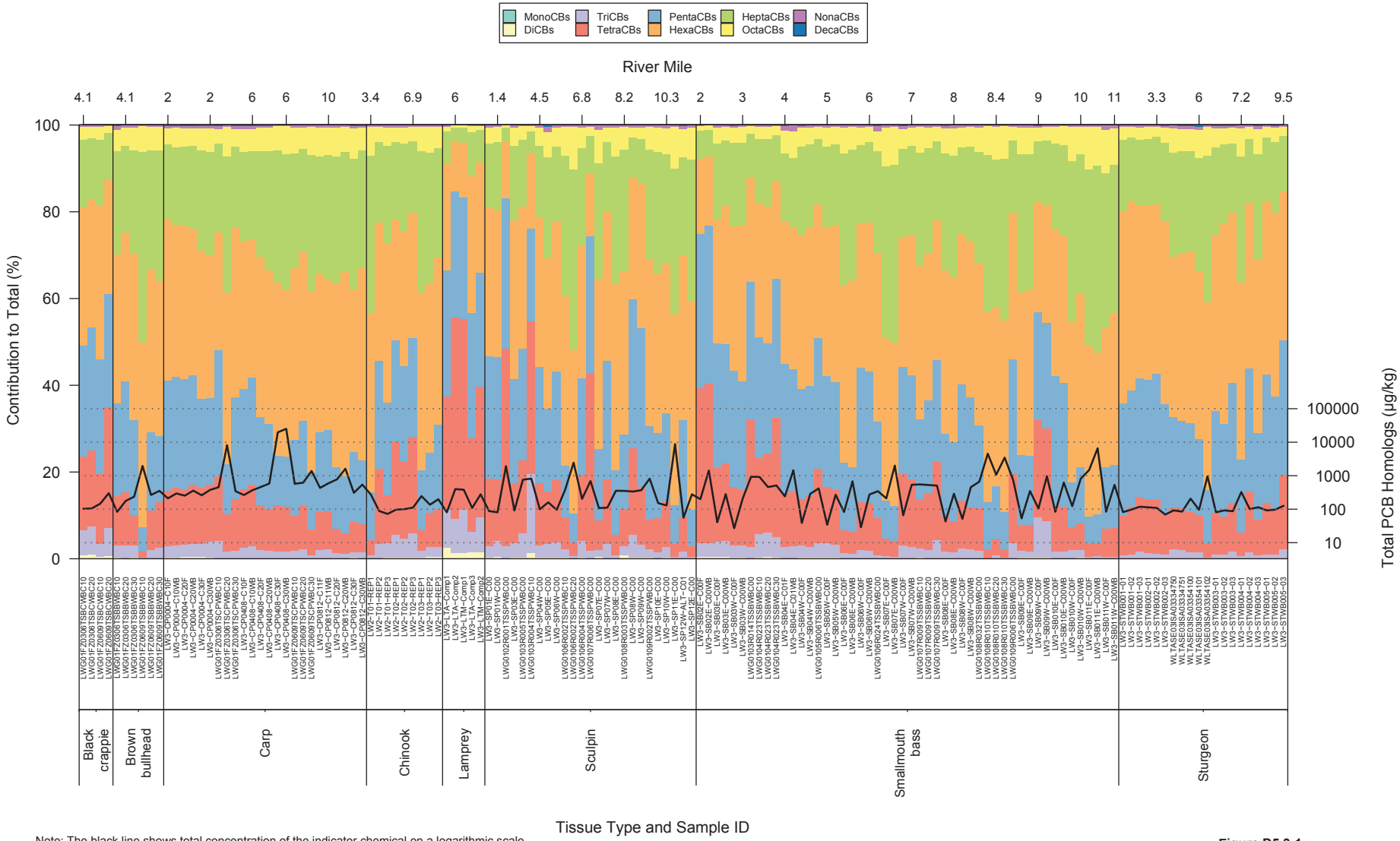
PAH data are available for only one clam sample that represents exposures upriver of the Study Area. HPAHs accounted for almost two-thirds of the total concentration in this sample.

D5.3.6 References

Tetra Tech. 2006. Dredge Material Management Plan Sediment Characterization Report Lower Willamette River Federal Navigation Channel, OR. WLCDRD05. Prepared for the U.S. Army Corps of Engineers, Portland District, Portland, OR. Tetra Tech EC, Inc., Portland, OR. January 2006.

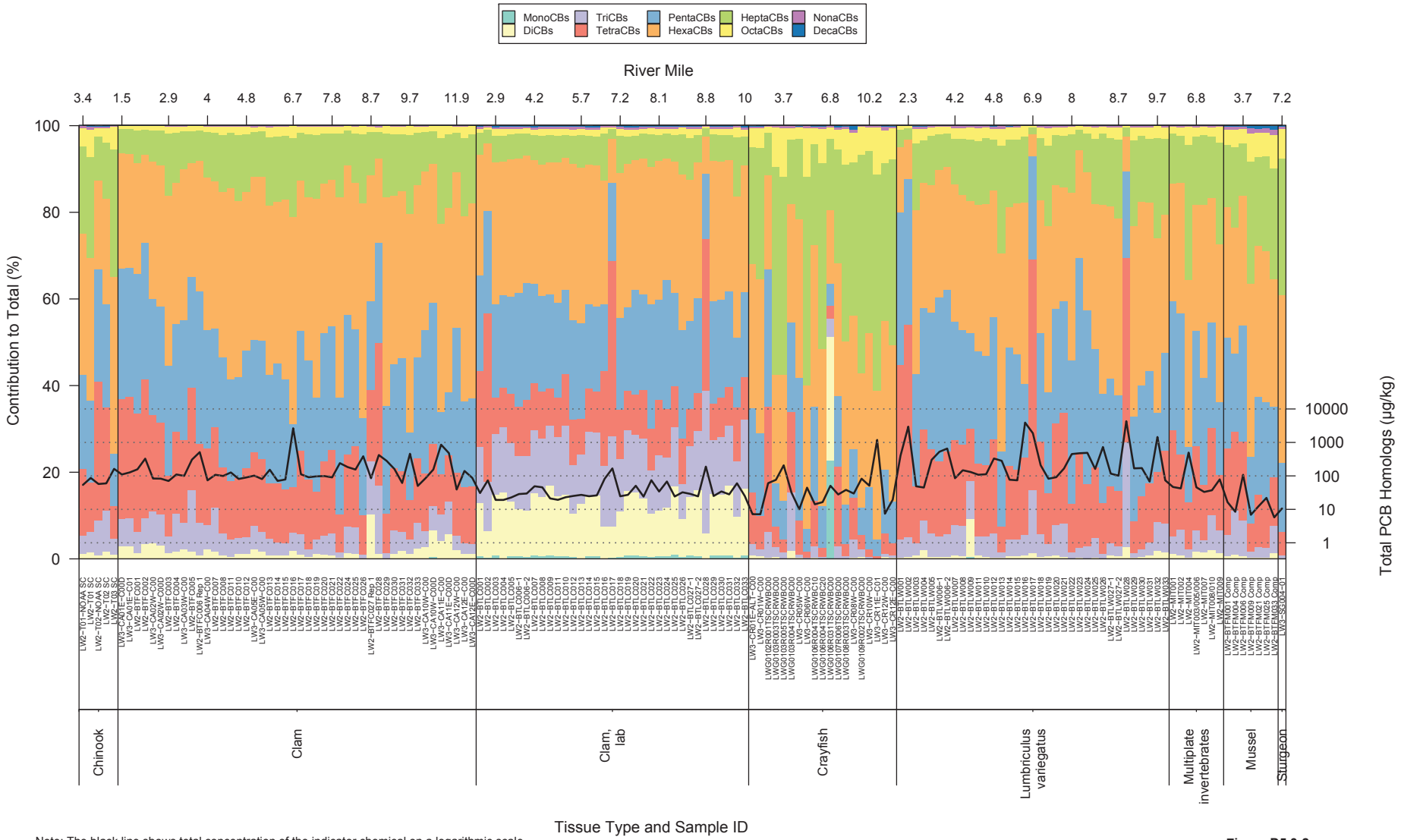
ODHS, USEPA, and ATSDR. 2003. Salmon, Sturgeon, and Lamprey Tissue Investigation, Portland Harbor Site. WLTASE03. Prepared for Oregon Department of Health Services, Portland, OR, U.S. Environmental Protection Agency Region 10, Seattle, WA, and U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, GA. 2003.

FIGURES



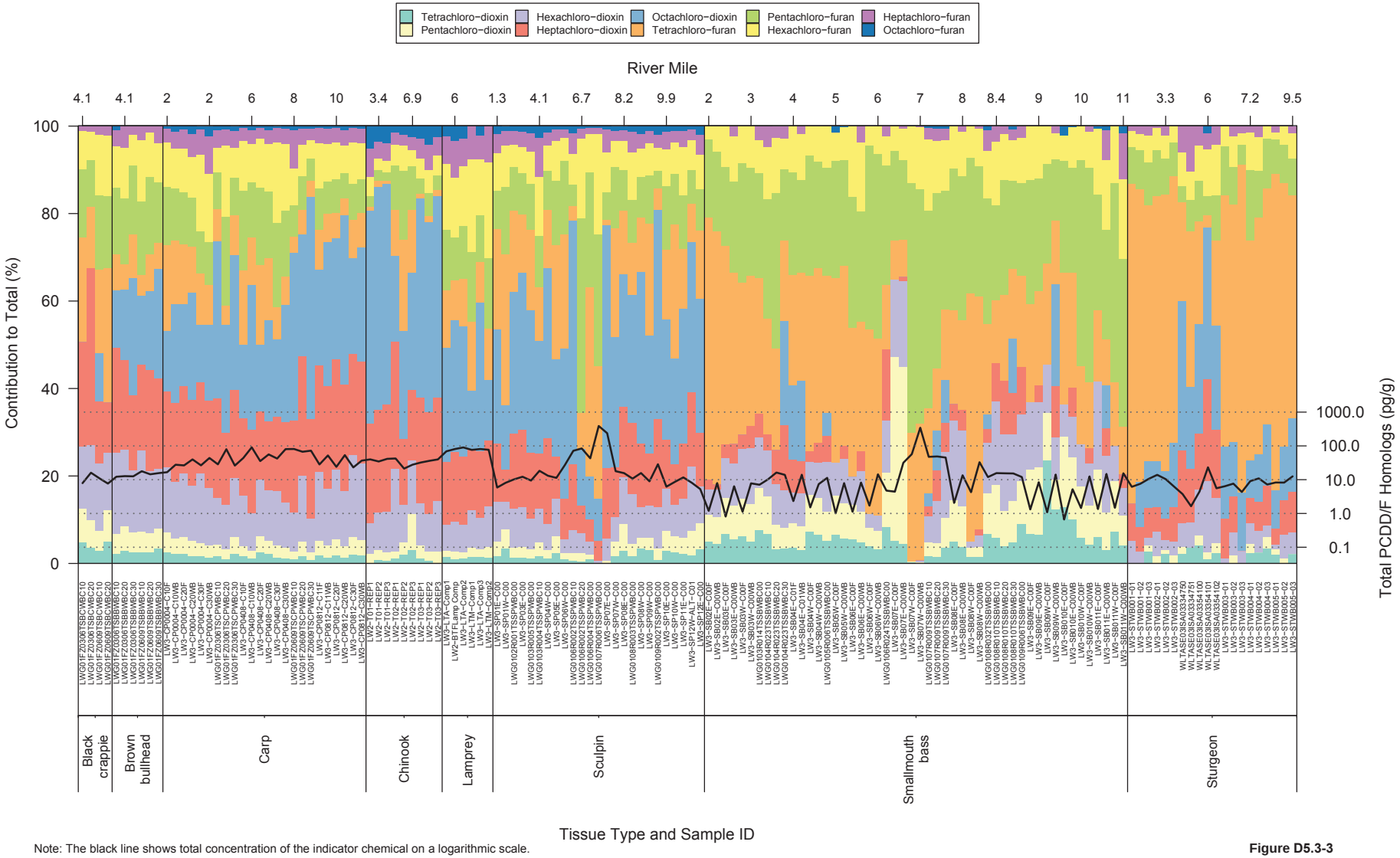
Note: The black line shows total concentration of the indicator chemical on a logarithmic scale.

Figure D5.3-1
Portland Harbor RI/FS
Remedial Investigation Report
Stacked Bar Chart of PCB Homolog Patterns
in Fish Tissue (RM 0.8 to 12.2)



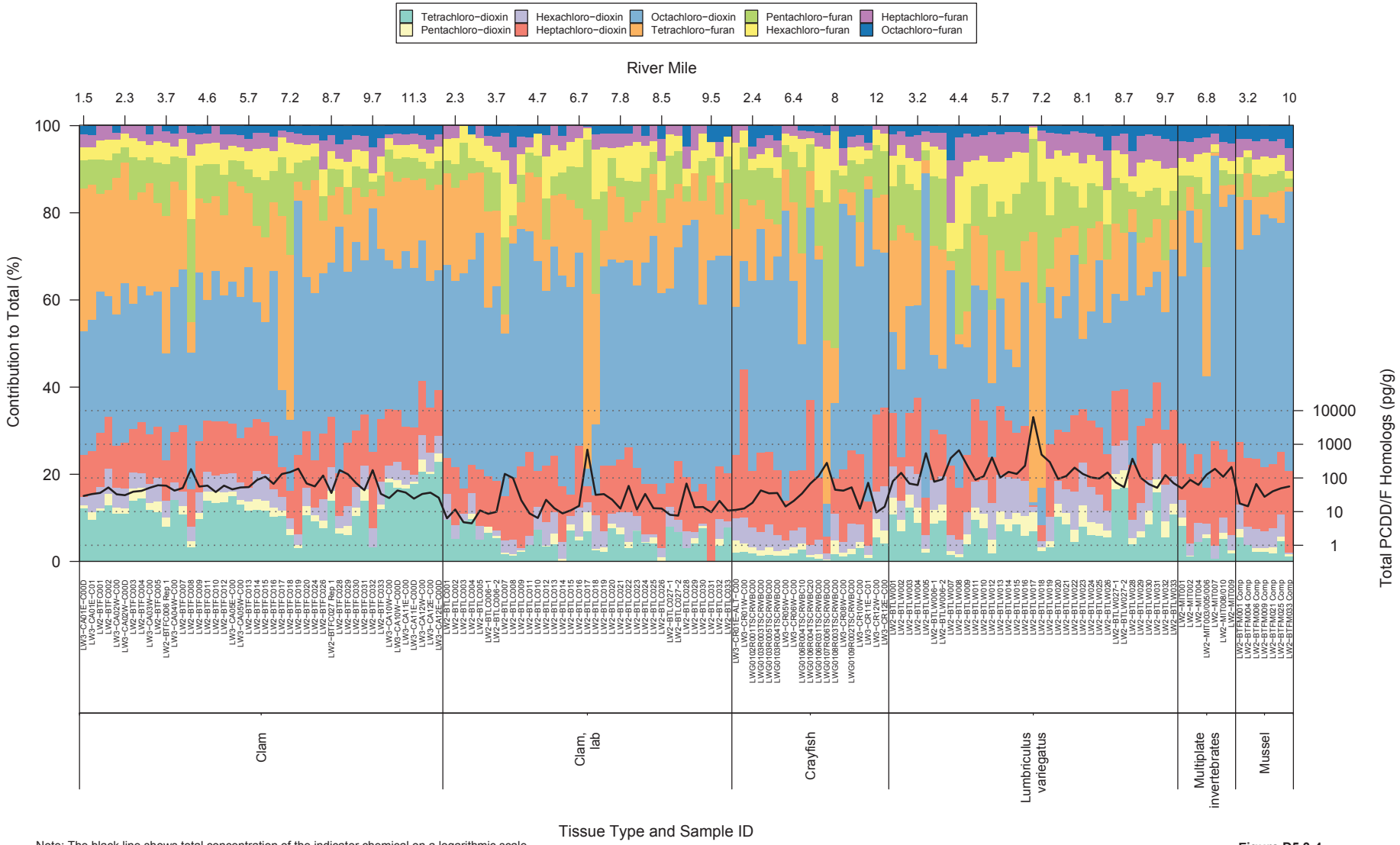
Note: The black line shows total concentration of the indicator chemical on a logarithmic scale.

Figure D5.3-2
Portland Harbor RI/FS
Remedial Investigation Report
Stacked Bar Chart of PCB Homolog Patterns
in Invertebrate Tissue (RM 0.8 to 12.2)



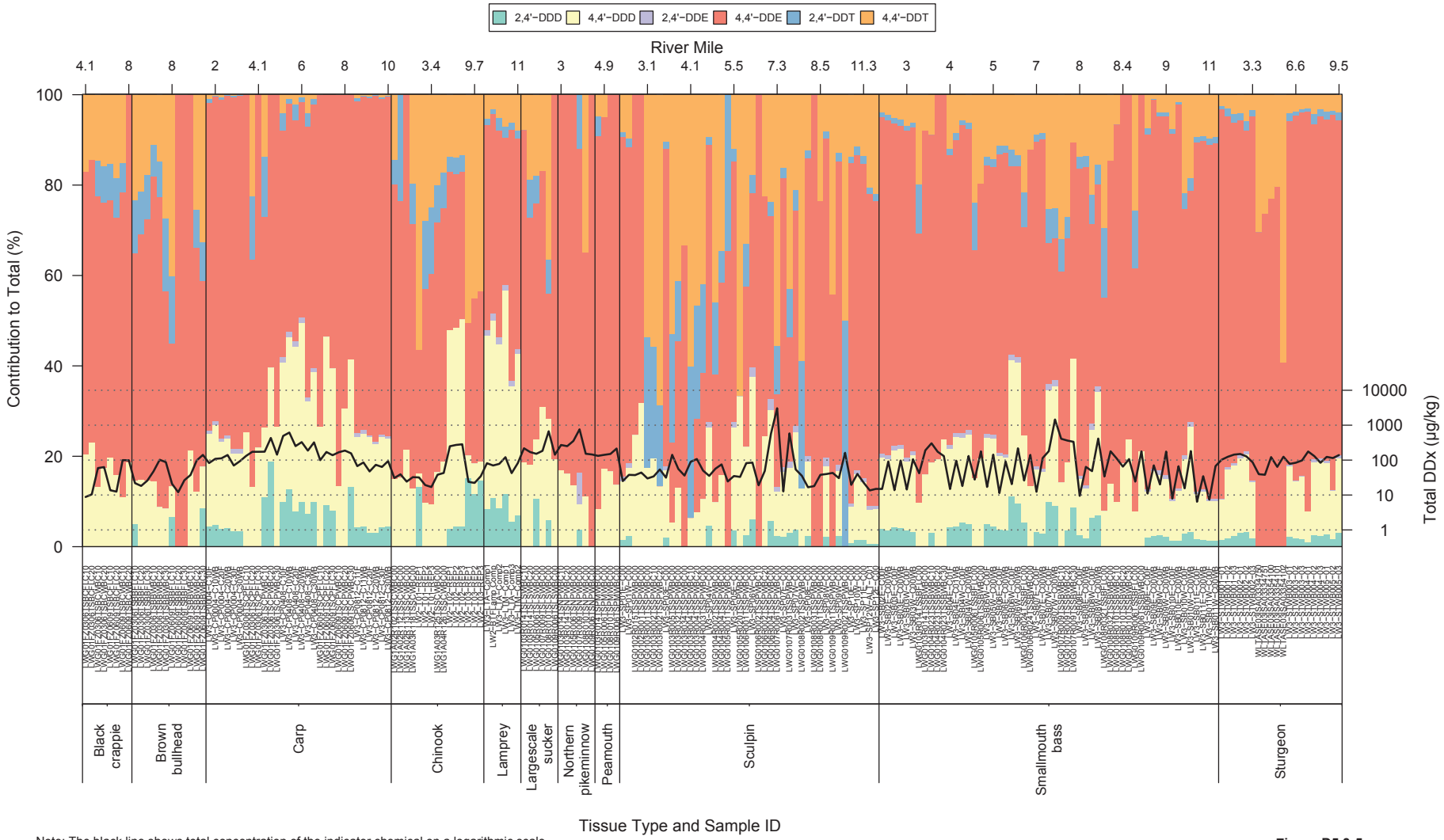
Note: The black line shows total concentration of the indicator chemical on a logarithmic scale.

Figure D5.3-3
Portland Harbor RI/FS
Remedial Investigation Report
Stacked Bar Chart of PCDD/F Patterns
in Fish Tissue (RM 0.8 to 12.2)



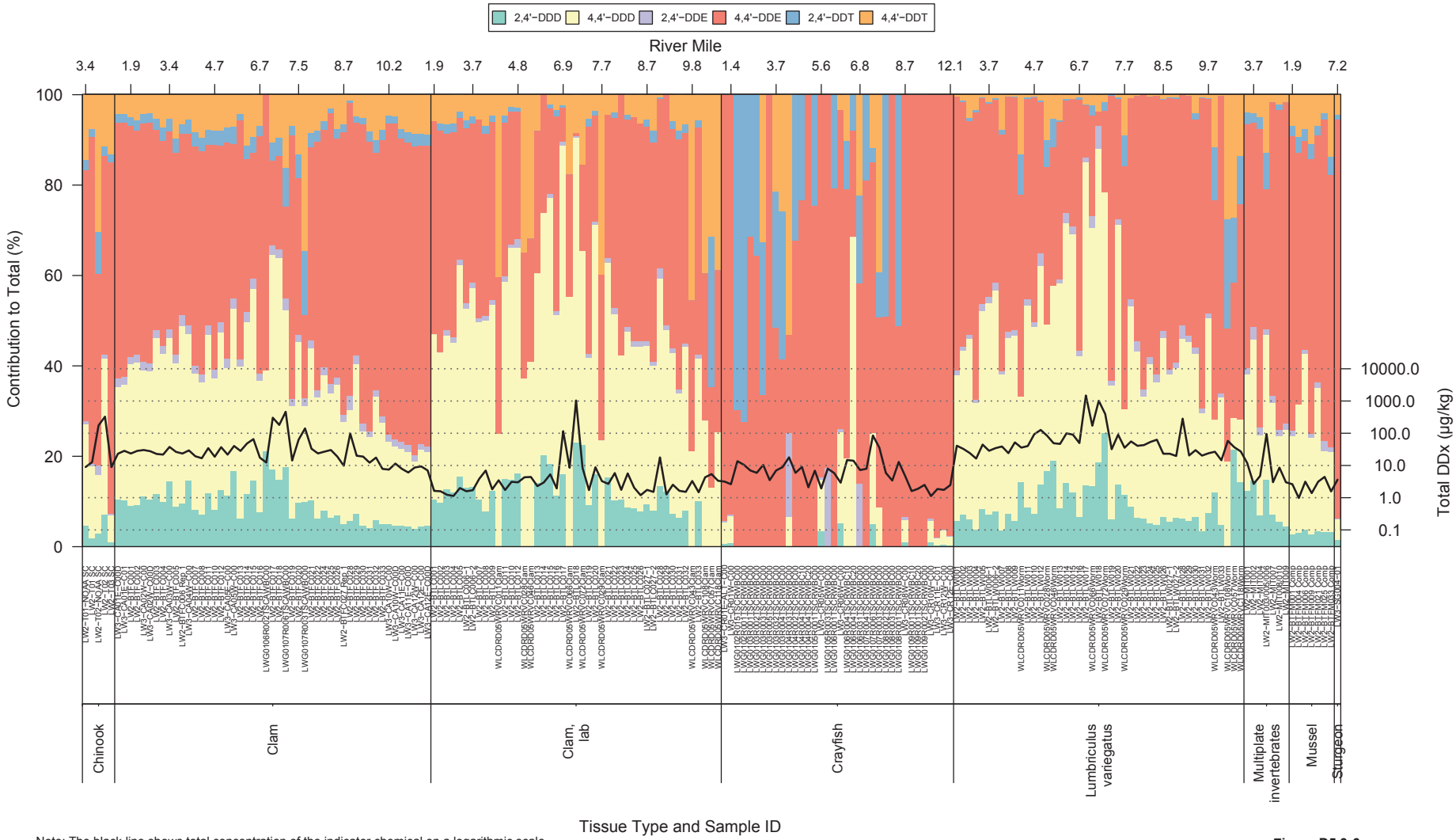
Note: The black line shows total concentration of the indicator chemical on a logarithmic scale.

Figure D5.3-4
Portland Harbor RI/FS
Remedial Investigation Report
Stacked Bar Chart of PCDD/F Patterns
in Invertebrate Tissue (RM 0.8 to 12.2)



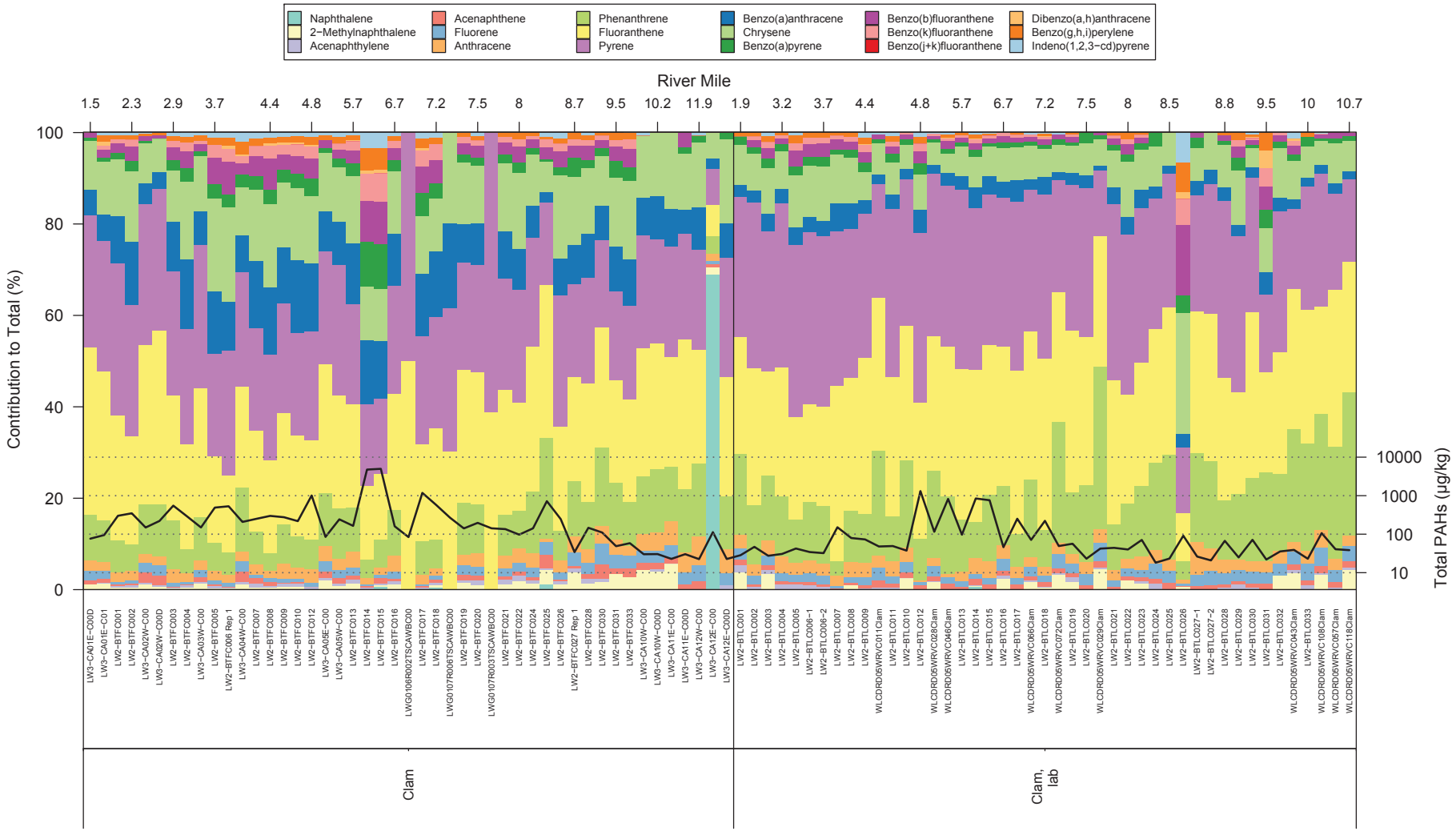
Note: The black line shows total concentration of the indicator chemical on a logarithmic scale.

Figure D5.3-5
Portland Harbor RI/FS
Remedial Investigation Report
Stacked Bar Chart of DDx Patterns
in Fish Tissue (RM 0.8 to 12.2)



Note: The black line shows total concentration of the indicator chemical on a logarithmic scale.

Figure D5.3-6
Portland Harbor RI/FS
Remedial Investigation Report
Stacked Bar Chart of DDx Patterns
in Invertebrate Tissue (RM 0.8 to 12.2)



Note: The black line shows total concentration of the indicator chemical on a logarithmic scale.

Figure D5.3-7
Portland Harbor RI/FS
Remedial Investigation Report
Stacked Bar Chart of PAH Patterns
in Clam Tissue (RM 0.8 to 12.2)